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Progress in Analytical Methods of Halogenated Disinfection By-Products

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Abstract: Ensuring the health and safety of drinking water is crucial for both nations and their citizens. Since the 20th century, the disinfection of drinking water, effectively controlling pathogens in water sources, has become one of the significant advances in public health. However, the disinfectants used in the process, such as chlorine and chlorine dioxide, react with natural organic matter in the water to produce disinfection by-products (DBPs). Most of these DBPs contain chlorine, and if the source water contains bromine or iodine, brominated or iodinated DBPs, collectively referred to as Halogenated disinfection byproducts (X-DBPs), are formed. Numerous studies have found that X-DBPs pose potential risks to human health and the environment, leading to widespread concern. Mass spectrometry has become an important means of discovering new types of X-DBPs. This paper focuses on the study of methods for analyzing X-DBPs in drinking water using mass spectrometry.

Keywords: Halogenated disinfection by-products; Drinking water; High-resolution mass spectrometry

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1. Introduction

In toxicological research, it has been extensively proven that most halogenated disinfection by-products (X-DBPs) possess significant genotoxicity, mutagenicity, and teratogenic effects, including carcinogenicity, teratogenicity, and mutagenicity. These characteristics imply that the accumulation and metabolism of X-DBPs in the human body may cause direct or indirect damage to the genetic material of cells, leading to cellular dysfunction, altered gene expression, or genetic mutations, which could ultimately result in cancer, reproductive system deformities, and other diseases [1]. Particularly concerning is the long-term intake of these X-DBPs by humans, even at very low concentrations, which may pose serious health risks due to bioaccumulation. X-DBPs can enter the human body through various pathways, such as the respiratory tract, the digestive system, and the skin [2]. In our daily lives, it is inevitable to come into contact with X-DBPs, as we rely on tap water to meet our drinking and other water needs. This reality has sparked widespread concern about X-DBPs.

In 2022, China revised the “Standards for Drinking Water Quality” (GB 5749-2022), specifically setting limits for various X-DBPs. Among them, trihalomethanes, bromodichloromethane, dibromochloromethane,

tribromomethane, dichloroacetic acid, and trichloroacetic acid, these six types of X-DBPs were adjusted from non-conventional to conventional indicators. This revision underscores the nation's heightened concern for the issue of X-DBPs and the recognition of their importance to public health. This measure aims to ensure stricter regulation of drinking water quality, thereby reducing the potential health threats posed by X-DBPs. Globally, many countries have recognized the hazards of X-DBPs and have implemented a series of stringent management and control strategies to reduce the concentrations of these harmful substances in drinking water and other water bodies. These control measures include the establishment of stricter water quality standards and improvements in water treatment processes to reduce the formation of X-DBPs. However, despite these efforts, the current control of X-DBPs, relative to their widespread presence in the environment, still appears to be insufficient. According to some research reports, many aquatic environments still contain a large number of X-DBPs that have not been detected or reported, indicating that existing monitoring and management measures are far from covering all potential X-DBPs comprehensively [3]. Furthermore, considering the complexity and diversity of X-DBPs, current detection technologies and methods may not fully identify and quantify all types of X-DBPs, leading to blind spots in the assessment of these substances. Therefore, enhancing research and developing more efficient detection techniques, as well as expanding the monitoring scope, are crucial for comprehensively monitoring and effectively controlling the environmental and health risks of X-DBPs.

1.1. Classification of halogenated disinfection byproducts

X-DBPs, classified according to the different halogen atoms they contain, can be divided into chlorinated, brominated, and iodinated disinfection by-products. The X-DBPs that have been more widely monitored to date include [4]:

(1) Trihalomethanes (THMs): These are formed when disinfectants react with natural organic matter in water. THMs are a group that includes chloroform, bromodichloromethane, dibromochloromethane, and bromoform. They are some of the most common disinfection by-products found in chlorinated water.

(2) Haloacetic acids (HAAs): Similar to THMs, HAAs are formed through the reaction of disinfectants with precursors in water. This group includes monochloroacetic acid, dichloroacetic acid, trichloroacetic acid, monobromoacetic acid, and dibromoacetic acid, among others.

(3) Halonitromethanes (HNMs): These compounds, including chloropicrin (trichloronitromethane) and bromopicrin (tribromonitromethane), are formed by the reaction of nitrogen-containing compounds in water with disinfectants.

(3) Haloacetonitriles (HANs): These are nitrogen-containing disinfection by-products that include dichloroacetonitrile, dibromoacetonitrile, trichloroacetonitrile, and tribromoacetonitrile. They form through reactions similar to those producing THMs and HAAs.

(4) Haloketones (HKs): This group includes compounds such as 1,1-dichloro-2-propanone and 1,1,1-trichloro-2-propanone. They are formed by the reaction of disinfectants with precursors in water.

(5) Haloaldehydes (HALs): This category includes compounds like chloral hydrate (trichloroacetaldehyde), which are produced through similar reactions as other X-DBPs.

2. Gas chromatography and gas chromatography-tandem mass spectrometry

Since the early 1970s, chromatography and mass spectrometry have gradually become key techniques for the analysis of DBPs in drinking water. Gas chromatography-tandem mass spectrometry (GC-MS) plays a crucial role in this process, requiring the preparation of water samples through organic solvent extraction steps to meet

its analysis requirements. Furthermore, to detect DBPs at low concentration levels (ng/L to mg/L), sample concentration procedures are also necessary [5]. Especially for DBPs with weak acidity, non-polarity, and volatility, GC-MS provides an effective detection method. In some cases, derivatization and non-derivatization methods are employed to enhance detection sensitivity and accuracy. The compound libraries established based on GC-MS, provide effective analytical means for both controlled DBPs (such as THMs, HAAs) and many uncontrolled DBPs, facilitating qualitative and quantitative analysis, as well as screening and identification of some novel DBPs.

Inorganic halogenated disinfection by-products include cyanogen chloride, chlorite, chlorate, and bromate, which are primarily formed from the reaction of disinfectants with inorganic materials or as a result of oxidation processes in the disinfection treatment. The identification and control of these X-DBPs are essential for maintaining water safety and reducing potential health risks associated with water consumption. Different disinfection methods and water treatment strategies can influence the types and concentrations of X-DBPs formed, highlighting the need for comprehensive water quality management and monitoring programs.

With continuous advancements in mass spectrometry technology, instruments with higher sensitivity and resolution are becoming increasingly important in DBP research. High-resolution mass spectrometry (HRMS), such as Orbitrap-MS and Time-of-Flight Mass Spectrometry (TOF-MS), has rapidly developed and is widely applied. Postigo identified 11 different I-DBPs, including a novel I-DBPs, iodoethylene, using XAD resin to concentrate water samples and analyzing the extracts with GC-Orbitrap MS in full scan mode, utilizing high-resolution accurate mass information [6]. Kimura's team used GC-TOF MS in full scan mode, offering strong credibility for target analytes and a complete mass spectrum for unknown targets, validated in drinking water samples from three different water treatment plants. This mode conducted a quantitative study of 39 DBPs, including six types (haloacetaldehydes, haloketones, haloacetonitriles, halonitriles, iodo-trihalomethanes), and performed non-target screening analysis for two DBPs (N,N-dimethylacetamide, N-nitrosodibutylamine) [7]. Additionally, comprehensive two-dimensional gas chromatography (GC×GC)-qMS has been applied in the analysis and identification of DBPs. Zhang *et al*. combined GC×GC–qMS with an electron capture detector to screen and identify DBPs in ozone-disinfected water samples, screening 635 DBPs and preliminarily determining the structures of 12 Br-DBPs, proposing structures for 4 novel Br-DBPs. This research marked the first report and identification of eight Br-DBPs, including brominated phenylethylenes and brominated phenylacetonitriles [8].

3. Liquid chromatography and liquid chromatography-tandem mass spectrometry

While GC-MS is widely regarded as an effective analytical method for identifying DBPs in drinking water, it is mainly suitable for lower molecular weight DBPs. This is because the volatility of DBPs usually decreases with increasing molecular weight, making them unsuitable for GC-MS detection. Conversely, for higher molecular weight DBPs, liquid chromatography-tandem mass spectrometry (LC-MS) has shown better detection performance. Takino *et al*. used liquid chromatography-electrospray ionization tandem mass spectrometry (LC-ESI-MS) with large-volume mixed-sample injection to separate nine HAAs within 20 minutes, achieving detection limits ranging from 0.024 to 0.118 mg/L [9]. Lu and colleagues explored the formation of Br-DBPs in natural organic matter after ozone disinfection in the presence of bromides, using UPLC-HESI-Orbitrap to collect sample information, successfully detecting 127 Br-DBPs and identifying 17 structures, 15 of which were reported for the first time [10]. Carter *et al*. combined LC-HRMS and SPE-LC-MS/MS to identify potential DBPs from chloramination of phenylalanine, identifying 16 out of 17 new DBPs and validating three using

standards, one of which was a Cl-DBP [11]. Additionally, derivatization followed by LC-MS identification of unknown DBPs has been applied. Derivatization, a method to enhance LC-MS detection sensitivity by increasing the molecular weight of the analyte above the chemical background threshold, involves extracting and pre-concentrating polar compounds and introducing easily ionizable groups. An example is the study by Steven *et al*., who derivatized water samples with dinitrophenylhydrazine (DNPH) before high-performance liquid chromatography (HPLC) analysis, effectively pre-concentrating high-polarity DBPs from ozonated drinking water, significantly improving detection sensitivity in both positive and negative ion modes [12].

4. Conclusion

Based on the above situation, it can be seen that with the advance of advanced high-resolution mass spectrometry technology, the detection and identification of X-DBPs have made remarkable progress. Nevertheless, research in the X-DBPs field still faces some challenges. Existing research indicates that the X-DBPs currently identified represent only a small fraction of these substances present in water bodies. SWATH model, as a mass spectrometry method with high throughput and high sensitivity, has been widely used in the study of proteomics and metabolomics, providing comprehensive and accurate quantitative analysis of macromolecular components in complex biological samples. However, the application of this technology in the detection of DBPs, especially X-DBPs, is relatively small. In view of the significant advantages of SWATH technology in terms of quality resolution and data acquisition efficiency, it has the potential to be further developed and applied to the detection of X-DBPs in environmental samples.

Therefore, establishing mass spectrometry methods for screening and identifying X-DBPs in drinking water is crucial for ensuring the safety and quality of drinking water and the rational use of chlorinated disinfectants. This paper aims to summarize the detection of X-DBPs through high-resolution mass spectrometry, to identify more X-DBPs, thereby providing important data support for the rational use of chlorinated disinfectants and safeguarding water quality safety.

Disclosure statement

The author declares no conflict of interest.

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